

Tensile Properties of Bristle Fibers Made from α - and β -Casein

N. J. Hipp, M. L. Groves, and T. L. McMeekin

Eastern Regional Research Laboratory, Philadelphia, Pennsylvania
Philadelphia, Pennsylvania*

Abstract

The tensile properties of fibers made from α - and β -casein and unfractionated casein have been compared. β -Casein fiber, oriented by stretching, was considerably better than the other casein fibers, and values for its wet and dry tenacity compared favorably with corresponding values for wool. The better fiber properties of β -casein are ascribed to its molecular structure.

CASEIN is an important industrial protein having many uses, such as for making coatings, adhesives, and fibers. Textile fiber made from casein has reached large-scale production in several countries [2, 4, 9, 20]. The preparation of a bristle fiber made from casein has also been described [16], and the method has been made commercially available [1]. The low tensile strength and brittleness of casein fibers have limited their commercial value [3]. The low tensile properties of commercial casein fibers can be ascribed to a number of possible causes, such as

heterogeneity, the presence of nonprotein impurities, and a low degree of orientation.

Casein is a mixture of at least three proteins [17], and the development of a practical method for the separation of the two principal components, α - and β -casein [11], has made these pure proteins available for the production of fiber. Since α - and β -casein differ markedly in amino acid composition [6], solubility [10], acid- and base-combining capacity, viscosity, and density [12], it was expected that the mechanical properties of fibers made from these two caseins would also differ.

The present paper describes the tensile properties of bristle fibers made from α - and β -casein, and dis-

* A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.

cusses the relationship of these properties to molecular structure.

Material

The unfractionated casein was prepared from skim milk by acidification, as described by Hipp and co-workers [10]. α - and β -casein were separated from a good grade of commercial casein by the aqueous urea method [11].

Extrusion

For preparing small amounts of fiber, a sodium press was modified so that the die and plunger could be heated electrically. The die, with a hole 0.014 in. in diameter, was preceded by three graded stainless-steel sieves, which acted as breaker plates. The use of breaker plates permitted the extrusion of bristle fiber relatively free of air bubbles. Finely divided casein was mixed with water and allowed to swell for about 2 hrs. at room temperature in a closed vessel. Water contents of 40% and 42%, respectively, were found desirable for the extrusion of unfractionated and α -caseins, whereas β -casein, containing fewer polar groups [6], required only 31% water. Approximately 5 g. of the casein-water mixture was placed in the extruder cylinder and heated to 95°–100°C. The fiber, formed by extrusion into air, was wound on a drum rotating in water.

Hardening

The unstretched fibers were placed in 4% formaldehyde or 1% quinone solutions at room temperature, under slight tension to prevent curling, for 20 hrs. The stretched fibers were partially hardened at room temperature by treatment with formaldehyde or quinone before being stretched in water. Fibers made from α -casein required 2 hrs. in 0.2% formaldehyde before being stretched, as compared with 3 hrs. for fibers made from unfractionated casein. It was found desirable to treat β -casein for 2 hrs. with 0.8% formaldehyde before stretching it. For the quinone-hardened fibers, a pretreatment of 1 hr. was required for α -casein and unfractionated casein fibers, whereas β -casein fibers required 1.3 hrs. in 1% quinone. Under these conditions, draw ratios (D. R. = ratio of final to initial lengths) of from 3 to 3.5 were obtained. Conditions of prehardening that would permit greater draw ratios did not result in improved tensile properties [16] or orientation, as shown by x-ray measurements [22]. The stretched fibers were then hardened under the same conditions as the unstretched fibers. After hardening, the fibers were

washed with water and air-dried, the stretched fibers being held in the stretched condition during drying.

Testing

Two machines* were used to study the tensile properties of the casein bristles. The Scott I-P-2 Serigraph, a constant-rate-of-loading machine set for 2-in. gage length, was used for tensile strength, and the Sookne-Harris autographic fiber tester [25], employing 1-in. specimens, was used for the stress-strain properties.

The denier of the fiber was determined by weighing 9 cm. of dry, conditioned fiber on a microtorsion balance. (The denier of the fiber = the weight (mg.) \times 100.) Dry-strength tests were made at 73°F and 50% relative humidity after the fibers had been kept under these conditions for 24 hrs. Wet-strength tests were determined after the weighed samples had been soaked in distilled water for 4 hrs. in individual test tubes. Soaking the bristle fibers for 4 hrs. was sufficient to attain equilibrium; further soaking gave essentially the same strength values.

All the strength values obtained with the Scott machine are averages of 10 tests. In the reported average values, results that were more than 10% lower than the average value of all tests were not considered in determining the tensile value. This is the method used by A.S.T.M. C-109-52 for the elimination of faulty specimens when relatively few test specimens are available. The dry knot test, which is a measure of brittleness, was made on tight knots according to A.S.T.M. D-258-48T. Since the dry knots were not prestressed, as reported by Susich [27], elongation measurements on knot tests were not considered. The dry knot test gives a measure of the "flexibility" of the fiber, which is expressed as the relative knot tenacity, in percent.

A constant rate of loading for the various denier fibers on the Scott inclined-plane tests was maintained by using the proper weight on the carriage to give 1 g./den./min. for full scale, which would approximate 2 g./den./min. for the fiber under test.

The Sookne-Harris fiber tester was modified by increasing its capacity with heavy chains to accommodate the load required to break the fibers. Only wet tests with the fiber immersed in water were made because it was not desirable to alter the capacity of

* Mention of these machines does not imply their endorsement or recommendation by the Department of Agriculture over other machines of a similar nature not mentioned.

the machine sufficiently to break dry specimens. The highest jaw speed of the machine, 0.2 in./min., corresponding to 20% elongation of the specimens per minute, could not be used because the recorded load fell behind the actual load in the straight-line portion of the stress-strain curve. Accordingly, the next highest jaw speed, 0.0885 in./min., was used, which corresponds to 8.85% elongation per minute. The fiber evaluation indices, as calculated by Smith [24], were used, except for the toughness index, which was calculated from the actual area under the stress-strain curve.

Results and Discussion

Table I gives the effect of orientation induced by mechanical stretching of partially hardened fibers on the tensile properties of α -casein, unfractionated

casein, 85% β -casein, and β -casein. The degree of orientation, as determined by x-ray, was highest for β -casein, which showed arcing in both the inner and outer rings. All the unstretched casein fibers, including the pure casein components α - and β -casein, showed the two diffuse rings of disorientated casein fibers, which have been illustrated by Happey and Wormell [7].

The dry and wet tenacities of all the various unstretched fibers (D.R. = 1.0) in Table I are about equal and of the same order as reported by Peterson and coworkers [19] and Diamond [3] for casein textile fiber. The increase in the wet and dry tenacities with the application of stretch confirms the findings of Nutting and coworkers [18] on orientated ovalbumin, and Diamond [3] on the stretched casein fiber Fibrolane B. The wet tenacity, however, was im-

TABLE I. EFFECT OF ORIENTATION ON THE TENSILE PROPERTIES OF CASEIN FIBERS

Hardening agent	Draw ratio† (D.R.)	Fiber diameter§ (mills)	Tenacity		Flexibility (%)	Elongation at break		Wet/dry tenacity ratio
			Dry (g./den.)	Wet (g./den.)		Dry (%)	Wet (%)	
<i>α-Casein (100%)</i>								
Formaldehyde	1.00*	10.0	.77	.19	87	7	32	.25
Formaldehyde	2.08	7.9	.93	.23	77	27	21	.25
Formaldehyde	3.0	6.7	1.06	.41	42	25	22	.39
Quinone	1.00*	10.6	.78	.26	88	5	57	.33
Quinone	2.15	8.5	.94	.37	75	14	34	.39
Quinone	2.98	6.9	1.17	.58	26	20	23	.50
<i>Unfractionated Casein (75% α- and 25% β-casein)</i>								
Formaldehyde	1.00*	11.8	.81	.24	89	7	53	.30
Formaldehyde	2.1*	8.7	.94	.32	48	17	31	.34
Formaldehyde	2.7†	8.6	.96	.31	36	18	21	.32
Quinone	1.00*	12.3	.75	.27	86	5	71	.36
Quinone	2.0†	8.4	.99	.39	50	15	34	.39
Quinone	3.2	7.1	1.21	.56	22	19	23	.46
<i>85% β- and 15% α-Casein¶</i>								
Formaldehyde	1.00*	11.5	.80	.25	81	7	42	.31
Formaldehyde	2.04	9.4	.95	.33	63	24	25	.35
Formaldehyde	3.7	4.4	1.01	.64	42	15	20	.63
Quinone	1.00*	10.8	.82	.29	78	5	50	.35
Quinone	2.1	8.9	1.01	.48	58	17	28	.48
Quinone	3.1	5.8	1.48	.75	23	16	17	.51
<i>β-Casein (100%)</i>								
Formaldehyde	1.00*	10.6	.81	.25	88	9	55	.31
Formaldehyde	2.0†	6.9	1.04	.40	50	21	30	.38
Formaldehyde	3.27	5.9	1.24	.78	26	16	25	.63
Quinone	1.00*	10.1	.81	.29	82	6	57	.36
Quinone	2.0	6.8	1.03	.52	76	21	38	.50
Quinone	3.13	6.3	1.26	.78	23	19	27	.62

* Average values of 3 extrusions.

† Average values of 2 extrusions.

‡ Ratio of final length to initial length.

§ Calculated from the average denier of the fibers by Sieminski's formula [23]; 1.29 was used for the density value of the fibers.

|| Ratio of dry knot tenacity to dry tenacity, in percent.

¶ Composition of the first β -casein fraction obtained with aqueous urea fractionation [11].

proved to a considerable greater extent than the dry tenacity, as shown by the increase in the wet/dry tenacity ratio. The increase in the dry and wet tenacities for unfractionated casein was about the same as reported by Diamond [3] for stretched casein textile fiber. The increase was greater for β -casein than for α -casein and unfractionated casein at comparable draw ratios. Pure β -casein and 85% β -casein showed the greatest improvement in dry and wet tenacities when the fiber was orientated by stretching. The best values in Table I are higher than we have been able to find in the literature for casein fibers, and are about the same as those reported for wool [3]. In general, a greater improvement is obtained with quinone-hardening than with formaldehyde-hardening of the fibers.

On stretching, the flexibility decreased markedly on both the quinone- and formaldehyde-hardened fibers. The same behavior was noted by McMeekin *et al.* [16] for quinone-hardened fibers at D.R. greater than 2.0; however, for D.R. less than 2.0, increased flexibility was obtained. A similar relationship between stretch, tenacity, and flexibility was obtained by Nutting and coworkers [18] with orientated ovalbumin fibers.

The decrease in the wet extensibility with increased strength and improved water-resistance of the stretched casein fibers is analogous to that found for oriented rayon. Sisson [14] pointed out that this may be due partly to a shifting of the amorphous regions, which are easily swollen and deformed, towards a more rigid crystalline state, where they are more strongly bound by polar forces and hydrogen bonds. The reactivity and extensibility of cellulose are thus associated with amorphous portions, whereas strength and elasticity are associated with the crystalline state. The dry extensibility of casein fiber, however, increases on orientation by stretching,

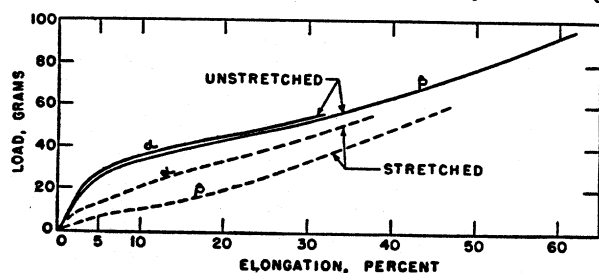


FIG. 1. Stress-strain curves for formaldehyde-hardened fibers while immersed in water at 73°F with a constant rate of elongation of 8.85%/min. Unstretched α -casein, 834 den.; unstretched β -casein, 644 den.; stretched α -casein (D.R. 2.64), 302 den.; stretched β -casein (D.R. 2.74), 222 den.

and is opposite to the behavior usually found for rayons [5, 14, 15]. The increase in the dry extensibility and the decrease in the wet extensibility have also been reported for the casein textile fiber Fibrolane by Happey and Wormell [7] and Entwistle [5]. Similar results have been reported for stretched ovalbumin fibers by Nutting *et al.* [18], who found that the dry extensibility increases to a maximum value and then decreases. The data in Table I indicate that the increase in dry extensibility might also reach a maximum value for casein, particularly β -casein.

Happey and Wormell [7] attributed the greater dry extensibility of the stretched casein fibers to the fact that the more folded and three-dimensional cross-linked chains of the unstretched fiber are more difficult to disentangle, and that fiber rupture takes place earlier than in the stretched fiber, where the chains are more extended and tend to unfold even further on stretching. The forces resisting extension in casein fiber when stretched in water were shown by Hoover, Kokes, and Peterson [13] to be rubber-like—i.e., the stress at a given elongation increases with an increase in temperature. These data may be interpreted as indicating an interaction between chains similar to that postulated by Happey and Wormell [7].

Stress-Strain Properties of α - and β -Casein Fibers

The stress-strain properties of α - and β -casein fibers immersed in water at 73°F and at a constant rate of elongation of 8.85%/min. are summarized in Table II and illustrated in Figures 1 and 2. The values in the table are average values, and the curves in the figures are the actual curves for individual fibers. The data given in the last three lines in Table II were obtained from hysteresis curves in which the fiber was elongated and relaxed in increments of 1% to 10% elongation, and then at 5% intervals to break. The fiber was loaded and unloaded at 8.85%/min.

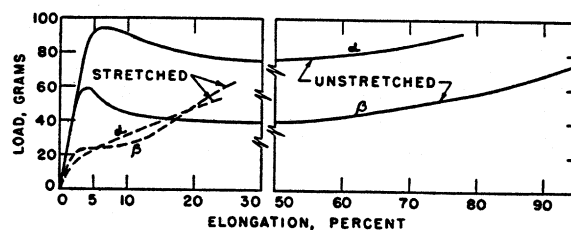


FIG. 2. Stress-strain curves for quinone-hardened fibers while immersed in water at 73°F with a constant rate of elongation of 8.85%/min. Unstretched α -casein, 995 den.; unstretched β -casein, 472 den.; stretched α -casein (D.R. 2.98), 186 den.; stretched β -casein (D.R. 3.13), 191 den.

The tenacity values in Table II are lower than those in Table I, a result expected from the known effect of the rate of loading on tenacity. The rate of loading with the constant-rate-of-elongation apparatus [25] used to obtain the data in Table II ranged from .1 to .4 g./den./min., compared with a constant rate of loading of 2 g./den./min. for the data in Table I. The lower wet tenacity at the low rate of loading is consistent with the low wet load at 20% elongation reported by Harris and Brown [8] for casein textile fiber (Table II).

Orientation by stretching of α - and β -casein fibers prehardened with formaldehyde or quinone affected the wet fiber properties in the following manner. The tenacity, modulus, stiffness, load at 30% elongation, and work recovery at 25% elongation increased; the elongation at break decreased; * the yield point was about the same for α -casein, but decreased for β -casein; the elasticity decreased, except for formaldehyde-hardened β -casein, the elasticity of which increased; the toughness index increased for formaldehyde-hardened fibers and decreased for quinone-hardened fibers; and the temporary set at 30% elongation was not changed by stretching. The data clearly demonstrate the improvement in fiber properties obtained by the orientation of α - and β -casein fibers induced by the stretching of the partially hardened fibers.

Stretched and unstretched quinone-hardened fibers

* The reported increase (Table II) for formaldehyde-hardened α -casein is for the single fibers given in Figure 1, but the average values on a number of tests showed a decrease in elongation at break.

from α - and β -casein have superior fiber properties, as compared with the formaldehyde-hardened fibers. The higher elongation at break for the stretched formaldehyde-hardened fibers is compensated in the quinone-hardened fibers by the greater tenacity, which is reflected in the toughness index and stiffness. The higher value for the temporary set for quinone-hardened fibers and the consequent lower work recovery value reflect the lower rate of elongation recovery for quinone-hardened fibers that occurs on the relaxation cycle, compared with that for formaldehyde-hardened fibers as deduced from the hysteresis curves. Under test conditions which would compensate for the lower rate of relaxation recovery for quinone-hardened fibers, the temporary set of these fibers would approach the value for the formaldehyde-hardened fibers, which is in agreement with the values reported by Harris and Brown [8] for 20% elongation.

The quinone-hardened fibers have a considerably greater modulus than the formaldehyde-hardened fibers. The value found for formaldehyde-hardened casein fiber is in agreement with the reported value of 0.016 [8]. In view of the correlation of resilience with work recovery and modulus, as established by Ray [21], the greater modulus, or resistance to deformation, for quinone-hardened fiber is significant. Harris and Brown [8] demonstrated that, with a decrease in cystine content, wool fibers stretched in water show diminished resistance to elongation as well as decreased modulus of elasticity. Since the cystine content is a direct measure of the number of disulfide cross-links, this finding demon-

TABLE II. STRESS-STRAIN PROPERTIES OF WET α - AND β -CASEIN FIBERS

	Formaldehyde-hardened				Quinone-hardened			
	Unstretched		Stretched		Unstretched		Stretched	
	α	β	α	β	α	β	α	β
Draw ratio (D.R.)	1.0	1.0	2.64	2.74	1.0	1.0	2.98	3.13
Yield point (g./den.)	.020	.071	.028	.026	.086	.119	.082	.085
Tenacity (g./den.)	.07	.12	.19	.26	.17	.17	.30	.36
Elongation at break (%) (values from Figures 1 and 2)	32.	62.	38.	46.	78.	96.	24.	26.
Modulus (g./den.) per % elongation	.0084	.0096	.013	.012	.027	.040	.041	.061
Toughness index (g./den.)*	.015	.033	.038	.054	.060	.093	.042	.047
Stiffness (g./den.) $\frac{\text{tenacity} \times 100}{\text{elongation} (\%)}$.21	.20	.49	.56	.22	.18	1.24	1.38
Elasticity (%) (elongation at yield point)	2.9	2.4	1.8	3.7	3.2	2.2	1.6	1.7
Work recovery (%)††	57.	63.	59.	71.	32.	33.	50.	49.
Temporary set (%)†§	10.	10.	9.	8.	18.	18.	16.	18.
Load at 30% elongation (g./den.)†	.045	.045	.126	.157	.067	.074	.269	.339

* Area under stress-strain curve to break.

† From hysteresis curves where the fiber was elongated in increments of 1% to 10% elongation, and then at 5% intervals to break.

‡ At 25% elongation, the area under the returning part of the curve, or work recovered, expressed as % work required to stretch the fiber.

§ At 30% elongation, when zero load is reached during constant rate of relaxation.

strates the dependence of mechanical properties such as modulus on cross-links. The higher modulus for wet quinone-hardened fibers may also be attributed to an increase in effective cross-links. Quinone, however, is not usually considered to be a cross-linking agent in the same sense as formaldehyde. The manner by which quinone increases the modulus may well be due to the deposition of quinone polymers in the fiber and not to chemical cross-links. Stoves [26] suggested that when human hair is boiled in aqueous benzoquinone to produce a "much less easily extensible" fiber, the role of the amino group in the formation of new linkages is demonstrated by the steadily diminishing formation of new linkages with increasing deamination of the fiber. Other experiments, as reported by McMeekin *et al.* [16], point to the probable availability of the ϵ -amino group of lysine for the reaction of quinone with proteins, but these reactions would account for only part of the total quinone that combines with casein. The modulus value obtained for quinone-hardened β -casein fibers approaches the modulus value of .10 for wet wool reported by Harris and Brown [8].

The superior wet stress-strain properties of fibers made from β -casein, particularly the quinone-hardened fibers, compared with fibers made from α -casein, are clearly demonstrated by the data in Table II. The same is true for the wet and dry tensile properties reported in Table I. That β -casein should form fibers with properties superior to those of α -casein might have been predicted from the viscosity values reported by Hipp *et al.* [12], who found that the volume fraction intrinsic viscosity and the axial ratio were greater for β -casein than for α -casein.

Recent preliminary determinations of the molecular sizes of α - and β -casein by Dr. Sam Sorof of The Institute for Cancer Research, Philadelphia, show that the sedimentation constants of the principal components of α - and β -casein are $S_{20} = 4.8$ and 13.3, respectively, in 0.15M NaCl at pH 6.9. These data indicate a molecular weight for α -casein of the order of 75,000–100,000 and for β -casein of 350,000, which are consistent with the viscosity values. The superiority of the β -casein fiber can therefore be attributed to the higher molecular weight of β -casein.

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